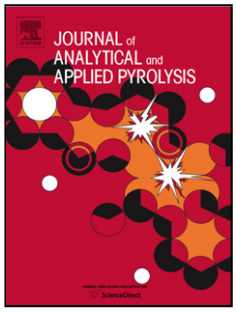

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Arsenic transformation behaviour during thermal decomposition of *P. vittata*, an arsenic hyperaccumulator

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Highlights

- As release and recovery have been clearly elaborated during pyrolysis and gasification of *P. vittata* in this study.
- The As concentration and speciation are determined by HPLC-ICP-MS.
- The As solubility in solid residue shows significant difference between low and high temperatures.
- The soluble As in solid residue mainly presents as As^{5+}.

Abstract: Thermal treatment of *P. vittata*, an arsenic hyperaccumulator harvested from contaminated land is a promising method of achieving volume reduction, energy production and arsenic (As) recovery simultaneously. In this paper, the arsenic transformation characteristics of field-harvested *P. vittata* were investigated during its pyrolysis and gasification process. The produced solid residue and flue gas were analysed by a high performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) to determine both the arsenic concentration and speciation. Moreover, the occurrence of arsenic in the solid residues was further identified as soluble and insoluble, which can feed information to the next arsenic recovery step. Results show that the fuel arsenic into gas phase increases firstly from 400℃ to 600℃, but then drops from 600℃ to 800℃, probably due to the self-retention of arsenic by CaO enriched in this *P. vittata*. Further increasing temperature to 900℃ will result in fast arsenic release. Gasification results in slightly higher arsenic release into the gas phase compared with pyrolysis.

Key words: hyperaccumulator, thermal treatment, arsenic, speciation, solubility

1. Introduction

Rapid industrialisation and economic growth in China has resulted in significant adverse effects on the environment. Heavy metal contamination in soil is of particular concern due to the scale of affected areas and significant public health risks [1-5]. According to a soil pollution survey [6] in China completed from 2005 to 2013 across 6.3 million km^2 of land area, 16.1% of sampling locations were found to have contamination levels exceeding the national soil limits. Among them, the majority (82.8%) are contaminated with heavy metals. Following this national soil survey, a Soil Pollution Control Action Plan was enacted on 28th May, 2016 by the central government of China to define clearly the requirements and goals of soil pollution control until 2030. Control of heavy metal pollution is emphasised within this plan [7].

Across the world, arsenic (As) is a widespread inorganic pollutant that causes significant problems due to its high level of toxicity [8, 9]. Arsenic and its compounds are confirmed environmental pollutant linked with high cancer rate after chronic exposure [10, 11] and recognised as carcinogens to human of highest potency by many health and environmental organisations including the International Agency for Research on Cancer (IARC) and US Environmental Protection Agency (EPA). The arsenic pollution in soil can originate from atmospheric deposition, irrigation with water from waste or polluted sources, uncontrolled release from mining and metallurgy industries [12]. In the latest national soil pollution survey in China, out of the 38,000 topsoil samples collected across 6.3 million km^2, 2.7% of the samples were found contaminated with arsenic at levels exceeding the national soil safety standard [6]. Significant proportion of these land areas surveyed are farmland used for food production, therefore there are growing concerns over food safety and human health [13, 14].

Conventional remediation technologies for organic pollutants including arsenic often involve soil excavation and removal or chemical stabilisation of pollutants by adding stabilising agents. In addition to these conventional methods, a plant based remediation technology, i.e. phytoremediation has gained significant interest in the last decade. The technology uses metal(loid) accumulating plants to remove soil contaminants therefore requires no significant energy input and it was widely accepted as a more sustainable remediation technology[15-24].

P. vittata is a well-known arsenic hyperaccumulator [17,18] and ideal candidate for arsenic phytoremediation. Since its discovery, field trials have been conducted by many labs to investigate the feasibility of using *P. vittata* in remediation of arsenic contaminated soil. In a number of field studies carried out in China, Chen et al. [19,20] reported the arsenic hyperaccumulation capacity of *P. vittata* and demonstrated the successfully application of this plant in arsenic remediation projects. Wang et al. [22] conducted arsenic phytoextraction experiments using ferns of the *Pteris* family indigenous to South China. The results showed *P. vittata* was capable of accumulating arsenic at more than 0.2% of its dry weight. The significant arsenic accumulation capacity of *P. vittata* was also reported in a number of other similar studies [23,24].

In China, field applications of *P. vittata* for arsenic phytoremediation have been demonstrated in Guangdong, Guangxi, Yunnan and the Hunan provinces where arsenic pollution are severe [25]. In a pilot study at a phytoremediation site in Chenzhou of Hunan province, it was found the annual yield of *P. vittata* biomass was nearly 4,400kg/hectare (dry weight) and the biomass contained

2.34% of arsenic (on dry weight basis) [19, 26]. The arsenic removal from the soil was therefore significant. However, it is a challenge to manage the large quantities of arsenic laden biomass economically and avoid further environmental pollution. A number of strategies for phytoremediation biomass waste management were proposed including direct extraction of arsenic and controlled incineration [27-31]. Amongst these methods, controlled incineration of phytoremediation biomass was considered as a feasible and economically acceptable method [31]. However, due to the low solid to gaseous phase transformation temperature, there are concerns over toxic emissions of gaseous arsenic during incineration process. Xie et al. [32] found that around 62.5% of arsenic in *P. vittata* volatilised below 400℃ during incineration. This was in agreement with the findings in combustion experiment of *P. vittata* using a muffle furnace carried out by Yan et al. [33] However, the behaviour of arsenic can be affected by many factors including operational parameters and the solid to gas transformation temperature depending on the biomass elemental compositions varies significantly. As an example, researchers showed that the volatilisation temperature of arsenic was higher than 1000℃ for coal and chromate copper arsenate (CCA) treated wood [34-36].

Many studies focus on reducing the gaseous emission of arsenic when treating phytoremediation biomass residuals. Pan et al. [37] proposed to use CaO to fix the arsenic in solid residue during incineration of *P. vittata*, then extracted by the NaOH-Na_2CO_3 solution, and finally precipitated by $CuSO_4$ solution to produce copper arsenate.

To date, there is limited scientific literature on the behaviour of arsenic during the thermal treatment process of *P. vittata*. Understanding this is crucial to ensure that arsenic is fixed in the solid residue so as to avoid volatile arsenic release into atmosphere. Also, predicting arsenic speciation in the solid residue is critical in achieving arsenic recovery in downstream process. In this paper, pyrolysis and gasification of high arsenic content, field-harvested *P. vittata* was undertaken to explain the behaviour and transformation of arsenic within these thermal processes.

2. Materials and Methods

2.1 Biomass Sample Preparation

The aerial parts of *P. vittata* were collected from an arsenic-phytoremediation field in Huanjiang of Guangxi Province in Southwest of China. Ultimate and proximate analysis was carried out following the Chinese Standard GB/T212-2008, GB/T476-2008, GB/T19227-2008 and GB/T214-2007. Biomass samples were dried at 70℃ for 2 hours to remove part of the moisture and facilitate the grinding, and then ground by a pulveriser before sieving through a 0.177mm mesh.

2.2 Experimental Setup

A series of experiments were designed and carried out in a horizontal tube furnace in order to grasp the transformation behaviour of arsenic during pyrolysis and gasification process of *P. vittata*. The experimental system included a gas cylinder, flow controller and meter, a horizontal quartz tube with a surrounding electrically heated furnace and a flue gas sampling line. Flue gas sampling was based on the USEPA-Method 29[38]. A schematic diagram of the sampling line is shown in Fig. 1. The length of the horizontal quartz tube was 1200mm with an inner diameter of 60mm, of which 400mm was isothermal and used as the reaction zone.

Ground *P. vittata* sample of 4g was weighed into a quartz boat using an analytical balance (Precisa LS120ASCS) with a readability of 0.1 mg. A sintered metal mesh was covered on the top of the quartz boat to prevent the potential solid elutriation. The quartz boat containing the sample was then loaded into the cold end of the furnace. Gas was introduced into the quartz tube from the start of the experiment with a fixed rate of 0.3L/min and the boat was moved to the centre of the reaction zone when it was pre-heated to the desired temperature. The sampling line between the furnace and condensate reservoir including the filter was heated by an electrical heater to 150℃. Preliminary tests were done to make sure that a 30min reaction time was adequate for the full conversion of the sample by weighing the solid residues. After each experiment, the 5%HNO_3+10%H_2O_2 solution used to trap the gaseous arsenic in the sampling line was collected for the ICP-MS analysis. After the furnace cooled down to room temperature, the solid residue in the boat was collected, weighed and sealed carefully. Temperatures ranging from 400℃ to 900℃ were tested and high purity N_2 (>99.99%) and CO_2 (>99.9%) were used to simulate the pyrolysis and gasification process.

1. Gas cylinder; 2.Valve controller; 3. Flow meter; 4.Temperature controller; 5. Thermocouple; 6. Insulation layer; 7. Horizontal quartz tube; 8. Quartz boat; 9. Fibreglass filter; 10. Condensate reservoir; 11. Absorption solution (5% HNO_3 + 10% H_2O_2); 12. Silica gel; 13. Ice bath; 14. Cold end; 15. Sintered metal mess.

2.3 Arsenic Analysis

The *P. vittata* and solid residue samples were digested following the Standing Committee of Analysts (SCA) standard method [39]. The samples were first digested in a HNO_3 and $HClO_4$ solution (analytical reagent, 4:1 HNO_3:$HClO_4$ by volume) and then extracted with the 7% (v/v) HCl solution. Both the arsenic concentration in these solutions and the collected absorption solution for gas phase arsenic were determined by the ICP-MS (ICP-MS-7900, Agilent Technologies Inc., USA). A group of 11 blank tests were completed and the detection limit of arsenic was 0.09μg/L. Each sample was detected 3 times and the average concentration was taken. In accordance with the standards, a relative standard deviation (RSD) of <5% was required for triplicate measurements. In the case of an outlier, the analysis was repeated until the defined accuracy was achieved.

The arsenic released into the gas phase was defined as the following equation [40]:

$$\text{Arsenic release(wt\%)}=\left(1-\frac{As_{res}m_{res}}{As_{dw}m_{dw}}\right)\times 100$$

Where As_{res} and As_{dw} denote the arsenic concentrations (mg/kg) in the residue and original sample, respectively. m_{res} and m_{dw} represent the mass(g) of the residue and original sample, respectively. The gaseous arsenic trapped in the absorption solution was not used directly since there might be some arsenic loss on the reactor wall and sampling line.

2.4 Arsenic Speciation Determination

The toxicity of arsenic compounds depends on their chemical form, e.g.As^{3+} is much more toxic than As^{5+}[41]. Therefore clarifying the transformation of arsenic speciation in the solid residues during the thermal treatment is of great significance. The solid residue was weighed to

0.01g and then digested by 10mL of 0.1%(v/v) HNO_3 to release the soluble arsenic fully. Arsenic that cannot dissolve in this low concentration HNO_3 solution was defined as insoluble arsenic in this research. The soluble arsenic in solution was then dissolved fully at room temperature in a ultrasonic bath (AS20500A, Auto Science, Tianjin) for 2 hours. Preliminary tests showed the majority (>95%) of the soluble arsenic dissolved within the first 5 minutes in the ultrasonic bath treatment, therefore the 2-hour extraction allows sufficient time for the complete dissolution of the soluble fraction of arsenic. The solution was centrifuged at 7000rpm for 10 minutes to obtain the supernatant, and the concentration of As^{3+} and As^{5+} were determined by the high performance liquid chromatography (HPLC, LC20-AB, Shimadzu, Japan) coupled with ICP-MS. The chromatograph used for analysis was a L20-AB (Shimadzu, Japan). The separation of As^{3+} and As^{5+} was achieved using the anion exchange chromatographic method with an analytical column (Hamilton PRP-X100) and anion chromatograph column of 250mm.The mobile phase consisted of 5mM ammonium phosphate ($(NH_4)_2HPO_4$) and 10mM ammonium nitrate (NH_4NO_3), the pH was adjusted to 7.0 and the flow rate was 1mL/min, the capacity of the quantitative loop was 200μl. The ICP-MS was coupled with HPLC through a Peek tube and the concentration of the separated As^{3+} and As^{5+} were determined respectively by the intensity curves from ICP-MS. Finally, the chromatographic quantitative calculation was conducted by the external standard method, i.e. by comparing the area of the As^{3+} and As^{5+}curve with the area of standard curve to determine the contents. The standard solution for arsenate and arsenite is reference material GBW08667 and GBW08666 in China, respectively.

3. Results and Discussion

3.1 Biomass Characterisation

Proximate and ultimate analysis include: moisture (M), ash content (A), Volatile matter (V) fixed carbon (FC), and CNHOS elemental compositions were determined. The results are summarised in table 1.

A detailed analysis of elemental contaminants in *P. vittata* biomass reveals a range of metal(loid)s absorbed by the plant, as shown in table 2. Among these elements, arsenic accumulation is the most pronounced at 318.39mg/kg. The arsenic concentration in the soil where the plants was grown was previously determined at 25.40mg/kg. This confirms the significant arsenic hyperaccumulating properties of *P. vittata*.

3.2 Arsenic release during pyrolysis and gasification

It is clear that pyrolysis and gasification reduce the sample weight of *P. vittata* efficiently, as shown in Fig.2. The weight of solid residue both decreased with increasing the temperature during both pyrolysis and gasification. At the beginning temperature of 400℃, about 50% weight reduction was achieved. The weight loss of gasification was always higher than that of pyrolysis, confirming the occurrence of gasification. The weight loss difference between gasification and pyrolysis went higher as temperature increased. At 900℃, the solid residue was about 18% of the raw material under gasification, indicating a nearly full conversion of the fixed carbon in the samples; while it was about 30% of raw material under pyrolysis.

The recovery of arsenic in the experiment was calculated by the percentage of the summation

of arsenic retained in solid residue and absorption solution. The arsenic content in the fly ash captured in the fibreglass filter was less than 1% of the total arsenic and it was not taken into account. Fig. 3 and Fig. 4 show the arsenic recovery during thermal treatment. It shows that more than 85% recovery ratio can be achieved for all the test runs. Reed et al. [42] pointed out that the mass balance ratio of 100±30% was normally satisfactory for trace element studies in pilot gasifier plants. Considering the analytical and experimental errors in testing and preparing the samples for ICP-MS analyses, the results were acceptable in this experiment. A relatively low recovery at lower temperatures was probably due to the arsenic loss with the deposit of tar formed at these temperatures on the sampling line.

Arsenic release shows a relatively complex trend in the pyrolysis and gasification process, as shown in Fig. 5. It first increased with temperature grow to 600℃ and then declines from 600℃ to 800 ℃ and dropped again when the temperature further increased from 800℃ to 900℃. At 600℃, around 60% of the arsenic was released under both pyrolysis and gasification process, which was in agreement with the former studies. Cuypers et al. [43] proved that the arsenic release showed a pronounced increase at temperatures higher than 390℃ in the pyrolysis of CCA treated wood. Yan et al. [33] in a complimentary study found that nearly 62.5% of the total volatilised arsenic emitted at the incineration temperature occurred below 400℃. It was reported that almost all arsenic in the *P. vittata* was present as relatively toxic inorganic forms, with little detectable organic arsenic species [18]. In another report, an unknown arsenic complex was also found in the *P. vittata* (Chinese brake fern) [44]. The volatility of the inorganic arsenic increases with increasing temperature. The compounds will decomposes to produce As_2O_5 or As_2O_3 when being heated, and As_2O_5 can easily decompose to As_2O_3 at 327℃[45-47]. As the boiling temperature of As_2O_3 is 457.2℃ [48] and the sublimation temperature is 135℃ [34, 49], As_2O_3 contributes a large proportion towards the total arsenic release before 600℃.

Arsenic release gradually decreased to around 45% from 600℃ to 800℃, then suddenly increased over 85% at 900℃ under both atmospheres. Discrepant results from Yan et al. [33] showed that arsenic release increase with increasing temperature from 600-800℃. A possible explanation for this was that the heating rate in the combustion experiments of Yan et al. was as low as 25K/min and the arsenic released continuously with the heating process. In contrast, in our study the heating rate was higher than 100K/s and thus volatilised arsenic would not have enough time to escape from the char matrix and could have been captured by other elements quickly [50, 51]. Table 3 shows the XRF analysis of the solid residue at 700℃ during pyrolysis and gasification. It is evident that the mass percentages of Mg, Ca, Al, Fe, Cr and Cu account for a large proportion of the total. These elements have the potential to react with arsenic to form some thermally stable compounds. Chen et al [52] has proved that increasing the temperature from 600 to 800℃ enhances the capture of arsenic by CaO. Therefore, whilst it is noted that arsenic release decreased from 600 to 800℃, this can be attributed to the formation of inorganic compounds and the fixation of arsenic in the ash matrix [53,54]. When the temperature exceeds 800℃, a fast arsenic release appeared. The falling of the thermal stability of inorganic compounds may be the reason for this [54-57]. The result shows that the composition of solid residues especially the alkali and alkali earth metal have a significant effect on arsenic release during thermal treatments. Moreover, arsenic release during gasification was a little bit higher than that of pyrolysis on the whole, which was probably due to the suppression effect on arsenic capture by CO_2. Under CO_2 atmosphere, some minerals such as limestone will not decompose to form metal oxides, which is the arsenic sorbents.

The physical adsorption of arsenic by char matrix will be also weakened, as the carbon content of the solid residue during gasification was lower than that of pyrolysis. The higher CO concentration in gasification can also reduce the As^{5+} to the less stable As^{3+}.

3.3 Arsenic speciation during pyrolysis and gasification

Figure 6 and 7 show the soluble and insoluble arsenic fraction in the solid residue during pyrolysis and gasification. It shows that most of the arsenic in solid residue was insoluble when the temperature was lower than 700℃, but more than 80% has become soluble when the temperature exceeds 800℃ both in pyrolysis and gasification. Taking the absolute amount of arsenic in the solid residues into account, it can be seen that the absolute amount of soluble arsenic at 400℃ is similar with that at 800℃ and 900℃, while the it is much lower at 500℃ – 700℃. $KAsO_2$ and KH_2AsO_4 are the commonly soluble inorganic arsenic forms and $Ca_3(AsO_4)_2$ is the most common insoluble form. It turned out that from 500℃ to 700℃, CaO captured the released arsenic species and fixed it as insoluble $Ca_3(AsO_4)_2$. But this assumption needs further verification.

Figure 8 and 9 show the $As^{5+}$and As^{3+}fractions of total soluble arsenic during pyrolysis and gasification. It is evident that the content of $As^{5+}$and As^{3+}has the same trend with temperature increase for both pyrolysis and gasification, and it shows that most soluble arsenic present as As^{5+}, and the content of soluble As^{3+} fluctuated with increasing temperature. It may be due to that oxygen contained within the fly ash supports the oxidation of arsenic, and this point is supported by Sterling and Helble's study[58] which showed that oxygen in reactants promotes arsenic oxidation and that CaO is capable of reacting with arsenic vapour species by forming calcium arsenates in the nitrogen atmosphere. Hu et al. [53] has also found that arsenic was in various phases and bound with calcite or Fe/Al oxides, and it was widely observed in MSW incineration that the large fraction of arsenic presented as As^{5+}. Moreover, the soluble As^{3+} increases with increasing temperature on the whole, no As^{3+} has been found below 600℃, a small part(less than 10%) presented as $As^{3+}$when the temperature ranged from 600-700℃, and the content of As^{3+} accounted for nearly 20% of the total soluble arsenic at the temperature exceeding 800℃. It is likely to be caused by the reduction of As^{5+} by carbon or CO during pyrolysis and gasification, and at higher temperature this reduction can become more pronounced.

4. Conclusions

This study provides new insights into the transformation of arsenic during the pyrolysis and gasification processing of *P.vittata*, a hyperaccumulator of arsenic. Results show that the transformation behaviour of arsenic has the same trend with increasing the temperature during pyrolysis and gasification. Nearly 60% of arsenic in the sample is released as the temperature reaches 600℃. This is likely to be due to the volatility of inorganic arsenic at lower temperatures. arsenic release then decrease between 600-800℃, which is likely to be due to the strong bonds between arsenic and the new generated char matrix. And increasing temperature to 900℃ will result in huge arsenic release, the rapid arsenic release and falling of the thermal stability of inorganic compounds in high temperature could be the proper reasons. Arsenic release during gasification is marginally higher than that of pyrolysis. Notably, most of the arsenic in the solid residue was insoluble at temperatures lower than 800℃, whereas nearly 90% of arsenic in the

solid residue became soluble during pyrolysis and gasification. And most of the soluble arsenic presented as As^{5+}.

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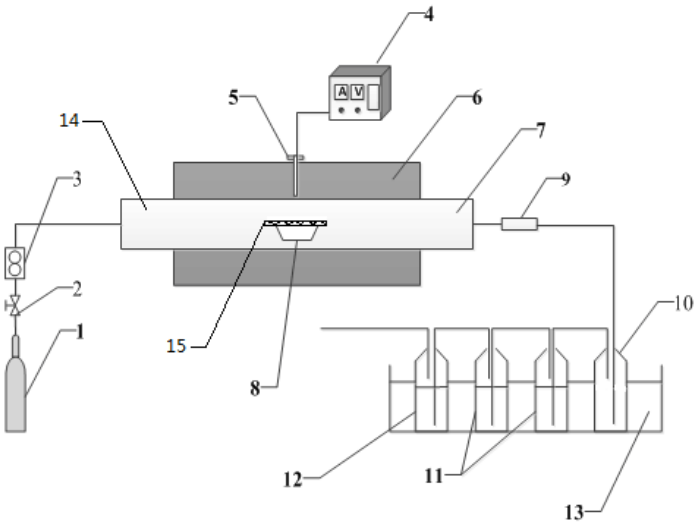

Fig. 1 Schematic diagram of the tube furnace

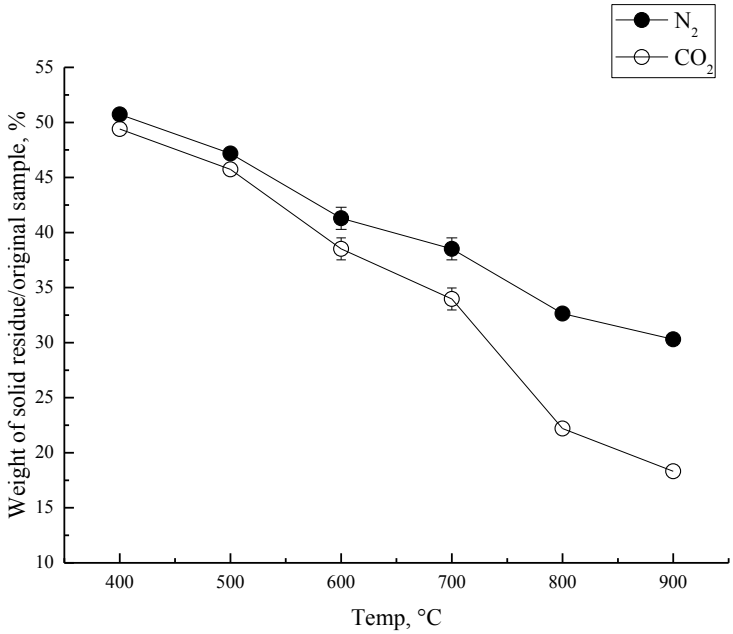

Fig. 2 Weight of solid residue during pyrolysis and gasification (%)

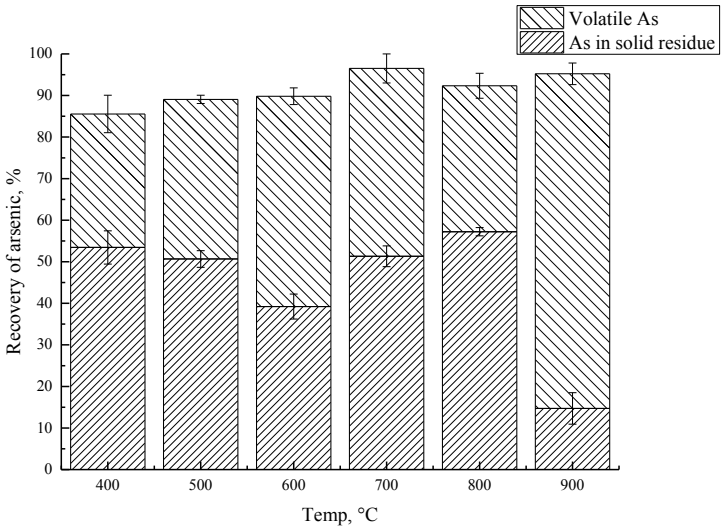

Fig. 3 Recovery of arsenic during pyrolysis (%)

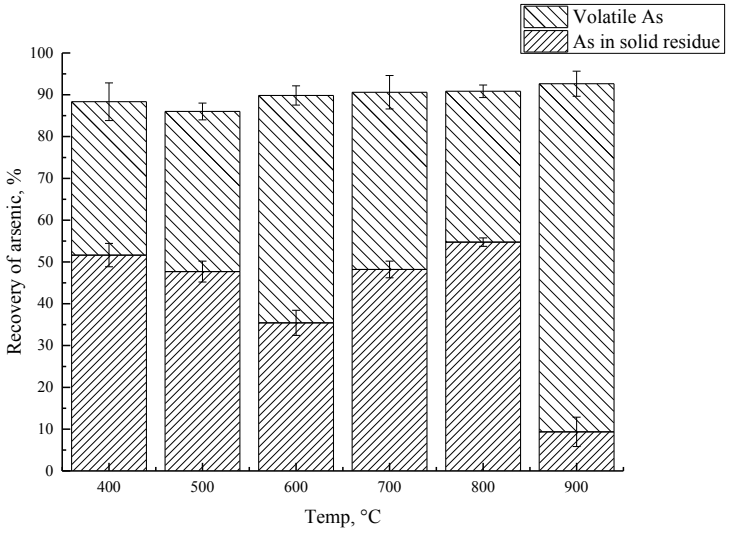

Fig. 4 Recovery of arsenic during gasification (%)

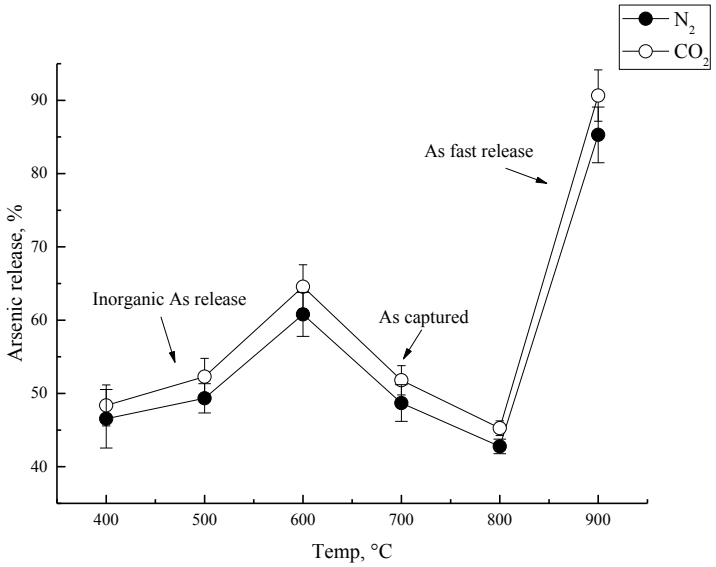

Fig. 5 Arsenic release during pyrolysis and gasification (%)

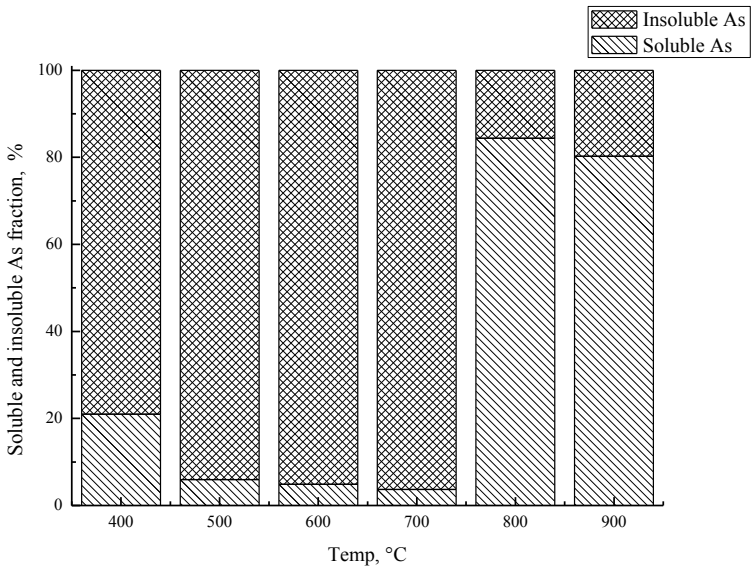

Fig. 6 Soluble and insoluble arsenic fraction in solid residue during pyrolysis (wt %)

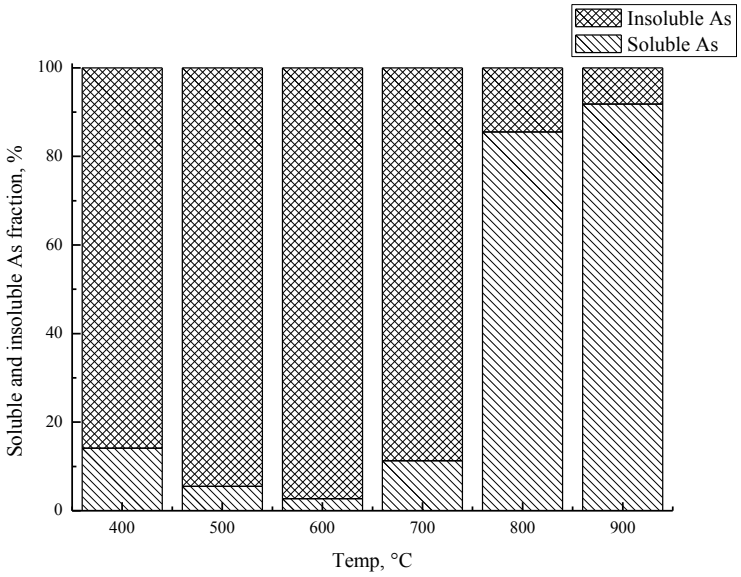

Fig.7 Soluble and insoluble arsenic fraction in solid residue during gasification (wt %)

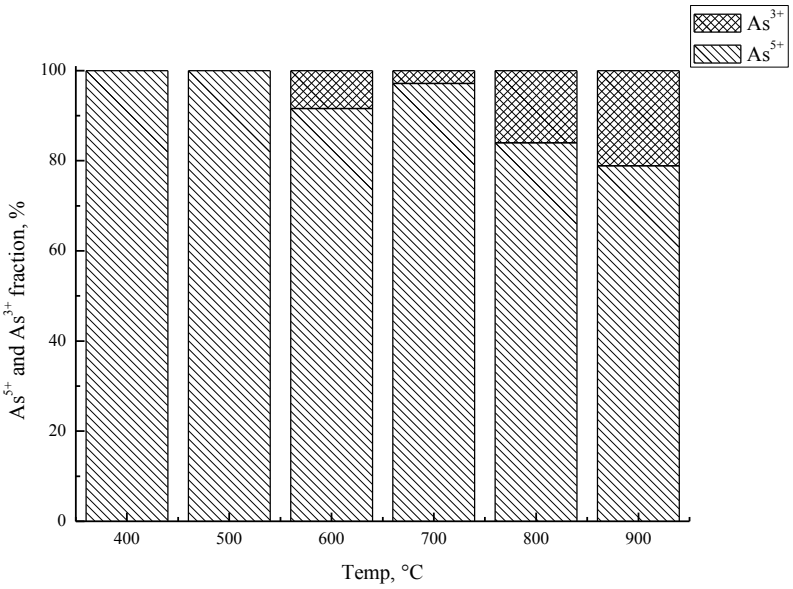

Fig. 8 $As^{5+}$and As^{3+}fraction of total soluble arsenic during pyrolysis (%)

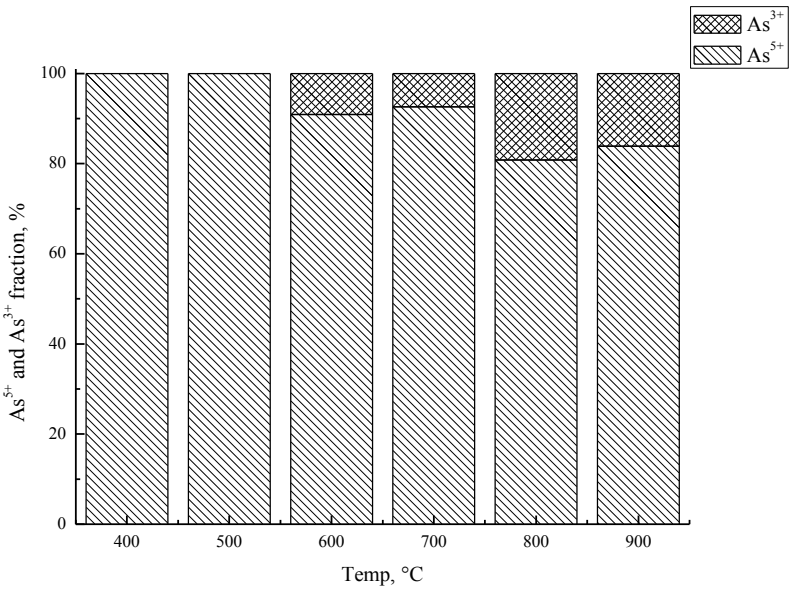

Fig. 9 $As^{5+}$and As^{3+}fraction of total soluble arsenic during gasification (%)

Table 1 Ultimate analysis and proximate analysis of the sample

Proximate analysis/%				Ultimate analysis/%				
M	A	V	FC	O	C	H	N	S
9.66	15.50	57.46	17.38	29.69	39.04	4.38	1.41	0.32

Note: all values are expressed on dry biomass basis

Table 2 Concentrations of the trace elements in the biomass sample (mg/kg, air dried basis)

Element	Cr	Mn	Co	Cu	As	Mo	Cd	Sb	Ba	Pb
Concentration	13.5	36.9	0.41	27.3	318.39	1.0	12.8	12.1	25.8	213

Table 3 XRF analysis of the solid residueat 700℃

N_2			CO_2		
Components	Mass%	LOD	Components	Mass%	LOD
Na_2O	0.24	0.02	Na_2O	0.21	0.04
MgO	4.90	0.02	MgO	5.21	0.02
Al_2O_3	2.92	0.01	Al_2O_3	2.66	0.01
SiO_2	28.55	0.01	SiO_2	30.97	0.03
P_2O_5	6.63	0.01	P_2O_5	6.23	0.01
SO_3	3.37	0.01	SO_3	3.00	0.01
Cl	3.19	0.01	Cl	3.48	0.01
K_2O	23.12	0.02	K_2O	20.44	0.01
CaO	24.44	0.02	CaO	25.52	0.02
TiO_2	0.31	0.02	TiO_2	0.34	0.03
Cr_2O_3	0.07	0.01	Cr_2O_3	0.09	0.01
MnO	0.06	0.01	MnO	0.03	0.01
Fe_2O_3	1.88	0.01	Fe_2O_3	1.49	0.01
CuO	0.05	0.01	CuO	0.06	0.01
ZnO	0.13	0.01	ZnO	0.10	0.01
As_2O_3	0.09	0.03	As_2O_3	0.09	0.03
Rb_2O	0.009	0.003	Rb_2O	0.007	0.003
PbO	0.04	0.01	PbO	0.07	0.01

(LOD: Limit of detection)